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Silicification of continental carbonates

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Abstract

The silicification of carbonate rocks is a diagenetic process that involves the major replacement of carbonate minerals by silica minerals (opaline phases, quartz and moganite), plus minor process of silica cementation in voids. When silicification is volumetrically significant, it generates silica rocks (cherts and opaline rocks) that stand out in carbonate outcrops as nodules, beds or lenticular beds, and other irregular accumulations. The silica required for this process may be obtained locally from siliceous components included within the carbonate rock (mainly siliceous microfossils, but also siliciclastic grains, clays and volcanic ash), or it may be transported from remote sites, generally by phreatic or hydrothermal water. During diagenesis, the opaline minerals of the siliceous microfossils (diatoms, spicules, phytholiths, etc.) are dissolved or recrystallized to quartz (ageing). The well-known opal A→opal CT→quartz transition releases silica and influences the diagenesis of the carbonates, producing generally silica-carbonate replacements, silica cementations or clay neoformations.

Silicification generally involves pseudomorphic replacement since the volumetric rate of silica precipitation is equal to the calcite dissolution rate. Thus, it tends to preserve information regarding the sedimentology, biota and diagenesis of the carbonate host-rock.

Most silicifications encountered in continental carbonates are interpreted as having occurred during the early burial diagenesis of lacustrine or palustrine sediments, or during meteoric diagenesis (the formation of silcretes and the silicification of palaeosols, calcretes and dolocretes). Currently, it is generally accepted that fluctuations in pH around a value of about 9 are a major controlling factor of silicification, since an inverse solubility relationship exists between calcite and silica. Changes in the salinity of pore fluids also induce silica precipitation. Other factors that affect silicification include the porosity of the carbonate rock and groundwater flow.

The time of silicification is difficult to establish, but can be defined in relation to: (1) the carbonate cementation and diagenesis of the carbonate host-rocks (physical and chemical compaction, dolomitization, dedolomitization, etc.), (2) the incorporation of fragments of silica rocks in younger formations, and (3) the characteristics of the silica rocks themselves (mainly the time of dewatering).

The oxygen and, to a lesser extent, the hydrogen isotope compositions of chert have been used to interpret the environmental conditions associated with quartz/carbonate replacement. If opaline phases are formed before quartz, however, no deductions regarding replacement can be made. Since most of the silicification of continental carbonates occurs in surface environments, the $\delta^{18}O$ and δD of the quartz formed usually record surface-water compositions, which are strongly influenced by evaporation and changes in salinity. When the silicification of the carbonates is synsedimentary or very early diagenetic, the isotopic composition of chert nodules can record the conditions of the sedimentary basin. In burial diagenesis, the chert isotopic composition can mark the thermal history of the carbonate host rock.

The study of the silica rocks (especially chert) formed by the replacement of carbonate rocks is an excellent tool for deducing many of the circumstances surrounding continental carbonate deposits and their diagenetic history.

Key words: Chert, Opaline rocks, Continental carbonates, Diagenesis

Resumen

La silicificación de carbonatos es un proceso diagenético que implica un proceso mayoritario de remplazamiento de minerales carbonáticos por minerales de la sílice (fases opalinas, cuarzo y moganita), así como un proceso minoritario de cementación de sílice en los huecos. Cuando la silicificación es importante volumetricamente se generan rocas silíceas (sílex y

rocas opalinas) que se destacan en los afloramientos de rocas carbonáticas, formando nódulos, capas, capas lenticular, y otras acumulaciones irregulares. La sílice necesaria para las silicificationes puede obtenerse de los componentes silíceos incluidos en la misma roca carbonática (microfósiles silíceos principalmente, pero también terrígenos silíceos, arcillas, cenizas volcánicas, etc.) o puede ser extraformacional, viniendo transportada por las aguas freáticas o hidrotermales. Los minerales opalinos que constituyen los microfósiles silíceos (diatomeas, espículas silíceas, fitolitos, etc.), durante la diagénesis, se disuelven o recristalizan a cuarzo. Esta recristalización, que implica las transformaciones opal A→opal CT→cuarzo, libera también sílice produciendo remplazamientos de carbonatos por sílice, cementaciones silíceas o neoformaciones de arcillas.

Generalmente en el proceso de silicificación sucede que el volumen de sílice precipitada es igual al volumen de calcita disuelta. Es un remplazamiento pseudomorfico, y por lo tanto, preserva las texturas y estructuras de la roca caja afectada facilitando información sobre la sedimentología, la biota y la diagénesis de dicha roca. La mayoría de los procesos de silicificación en carbonatos continentales se interpretan como procesos diagenéticos tempranos, durante el enterramiento de sedimentos lacustres o palustres, o durante la diagénesis meteórica (generación de silcretas o procesos de silicificación de paleosuelos, calcretes y dolocretes). Se acepta generalmente, que las fluctuaciones de pH alrededor de 9, son un factor desencadenante del proceso de silicificación, porque en este entorno de pH, existe una solubilidad inversa entre la calcita y la sílice. Cambios en la salinidad de los fluidos intersticiales de la roca carbonática, también inducen la precipitación de sílice. Otros factores que condicionan la silicificación son la porosidad de la roca carbonática y el flujo de agua subterránea.

El momento de la silicificación es difícil de establecer, pero en algunos casos puede ser definido por: (1) su relación con cementaciones carbonáticas y otros procesos diagenéticos de la roca caja (compactación física o química, dolomitización, dedolomitización, etc.), (2) haber sido erosionada la roca silícea y estar sus fragmentos incorporados en formaciones mas modernas, y (3) por las características estructurales propias de las roca silícea (momento de la deshidratación, principalmente).

La composición en isótopos de oxígeno e hidrógeno en sílex formados por cuarzo, se ha utilizado para interpretar las condiciones ambientales del remplazamiento cuarzo/carbonatos. Debido que la mayoría de las silicificaciones de carbonatos continentales se producen en ambiente superficial, los valores isotópicos de $\delta^{18}O$ y δD del cuarzo suelen registrar la composición de las aguas superficiales que están fuertemente influenciadas por la

evaporación y los cambios de salinidad. Cuando las silicificaciones son sinsedimentarias-diagenéticas tempranas, la composición isotópica de los nódulos de sílex que se forman puede indicar condiciones de la misma cuenca de sedimentación. En la diagénesis por enterramiento la composición isotópica del sílex, puede marcar la historia térmica de las rocas carbonáticas. El estudio de las rocas silíceas formadas por remplazamiento (y especialmente el sílex), es una excelente herramienta para deducir muchas de las circunstancias de los depósitos carbonáticos continentales que las incluyen, y su historia diagenética.

Palabras clave: Sílex, Rocas opalinas, Carbonatos continentales, Diagénesis

1. Introduction

The silicification of carbonate rocks is a diagenetic process that involves the major replacement of carbonate minerals by silica minerals (opaline phases, quartz and moganite), as well as a minor process of silica cementation in voids. When these processes are volumetrically significant, they generate silica minerals (chert and opal) that stand out in carbonate outcrops because of their greater resistance to weathering. Silica bodies occur as nodules, beds or lenticular beds, stringers and irregular accumulations (Fig. 1), and range in size from a few millimetres to many metres in length. They are found within carbonate beds (Fig. 1A-D) and along the bedding planes or their fractures - zones in which the fluids that precipitated the silica minerals were able to move (Fig. 1E-F). Chert and opal provide a showcase of carbonate host-rock history since silicification tends to preserve information on its sedimentology, biota and diagenesis.

The silicification of carbonates can be seen in Precambrian through Quaternary rocks, but data on the silicification of continental carbonates is more scarce than in marine environments. Most of the silicifications encountered in continental carbonates are interpreted as having occurred during the early burial diagenesis of lacustrine or palustrine sediments, or during meteoric diagenesis (the formation of silcretes and the silicification of palaeosols, calcretes and dolocretes). In a lake with carbonate deposition, Wells (1983) summarized four mechanisms of chert formation: (1) primary inorganic precipitation as a gel, (2) syngenetic to very early burial replacement of calcite, (3) late void filling after dolomitization and burial, and (4) early silcrete-like silicification. He thus indicated that there is no single solution to the "chert problem".

Some cherts are interlayered with continental carbonate rocks, but their genesis *sensu stricto* is not related to the diagenetic process that carbonates undergo, and they are not considered in this chapter. These cherts include the "Magadi-type cherts" from alkaline lakes (in the majority of cases representing the shallow-water diagenetic alteration of hydrous sodium silicate to silica) (Schubel and Simonson, 1990), "cauliflower cherts" (silica replacements of anhydrite/gypsum nodules in carbonates) (Milliken, 1979), and cherts/opal bodies formed by the replacement of thin levels of sepiolite interlayered with shallow continental carbonates (Bustillo and Alonso-Zarza, 2007).

2. Overview

2.1 Silica minerals and diagenesis

Silica rock is a general term used to define a rock composed mainly of SiO_2. In the strict sense, "chert" is used to define a silica rock made mainly of quartz plus small amounts of opaline minerals, whereas the term "opal" is used in the literature to represent both a mineral and a rock.

The opaline minerals are metastable and have different degrees of crystallinity, crystal structure and proportions of water. Jones and Segnit (1971) classified opal minerals into three groups, according to their X-ray diffraction (XRD) patterns: Opal A (with an XRD pattern that resembles that of amorphous silica), Opal C (which shows four moderately broad peaks that coincide closely with the position of the four most intense peaks of α-cristobalite, plus minor evidence of α-tridymite), and Opal CT (with patterns that show signs of both α-cristobalite and α-tridymite). Opal A can be inorganic, but is frequently found on siliceous microfossils (diatom frustules, sponge spicules, phytoliths, etc.). Opal C is very rare in sediments. Opal CT is the most common phase, but its structure can differ owing to its variable water content, the ratio of interlayered cristobalite/tridymite to amorphous background, and the degree of stacking disorder within the silica framework (Guthrie et al., 1995).

During burial diagenesis, opaline phases undergo successive dissolution-precipitation-recrystallization (ageing), including the well-known opal A→opal CT→quartz transition (Williams and Crerar, 1985; Williams et al., 1985). These transformations depend mainly on

time and temperature, but are accelerated when they occur in meteoric diagenesis, in which quartz crystals can form directly by bypassing the opaline silica polymorph phases (Arakel et al., 1989; Bustillo and Alonso-Zarza, 2007). The existence of opal CT in very young and surface rocks (Jones and Renaut, 2007) shows that time is not necessarily "a cause" of diagenesis. In continental environments, very rapid diagenesis appears to be related to efficient fluid delivery (i.e., hydrogeology) as much as to time.

When opal A or opal CT are included in carbonate rocks, their ageing sets silica free and influences the diagenesis of the carbonates, producing generally silica/carbonate replacements, silica cementations, or clay neoformations in the carbonate host-rock.

Quartz is the last stage of the recrystallization of opals, but it can also be formed directly in carbonates by their replacement or by the cementation of voids. Such quartz shows many textures under polarizing light. Common quartz can have different crystal sizes and forms crypto-, micro-, meso- or macrocrystalline mosaics. Maliva and Siever (1988) indicated that meso- and macrocrystalline quartz are not produced by ageing but only by direct precipitation during replacement or cementation. Chalcedony is a fibrous-texture quartz of different varieties: calcedonite (length-fast chalcedony, in which the elongation of the fibres is perpendicular to the crystallographic c-axis), quartzine (length-slow chalcedony, in which the elongation is parallel), lutecite (another type of length-slow chalcedony, in which the fibre axis is inclined by approximately 30º), and helicoidal calcedonite or zebraic chalcedony (which shows a systematic helical twisting of the fibre axes around the crystallographic c-axis). These varieties of chalcedony allow the identification of the environment reigning during the replacement or cementation as acid or non-sulphate (length-fast), or basic or sulphate/magnesium-rich (length-slow) (Folk and Pittman, 1971). The host material therefore has geochemical control over the textures of quartz precipitated. Unfortunately, there are exceptions to these rules and the strict application of these criteria can lead to errors of interpretation.

Moganite is a metastable monoclinic silica polymorph that is structurally similar to quartz (Miehe and Graetsch, 1992). The identification of moganite in the presence of quartz is difficult. It can be detected, however, by detailed XRD analyses with Rietveld refinements, and by other techniques such as Raman and NMR analysis. This mineral is found mixed with quartz in many cherts, preferentially in those that developed in evaporitic environments. However, it can also be produced by the replacement of biogenic carbonates during the interaction of the latter with groundwater (Heaney and Post, 1992). Moganite transforms into

quartz, as do the opaline phases, and it probably does so quite readily (Heaney and Post, 1992; Rodgers and Cressey, 2001).

2.2 The replacement process

A general geochemical and thermodynamic requirement for the silicification of carbonates is the existence of pore fluids that are supersaturated with respect to the silica phase precipitated, and undersaturated with respect to the carbonate mineral dissolved. (Hesse, 1989, among others). Any diagenetic fluid carrying more than 6 mg/dm^3 of dissolved silica can precipitate quartz. At values above 80 mg/dm^3 it is likely that opaline phases will precipitate instead (above 80 mg/dm^3 for opal CT, and above 120 mg/dm^3 for opal A) (Knauth, 1992). Silicification frequently represents a volume-by-volume replacement of calcite and/or dolomite, which allows the textural and structural characteristics of the carbonate rocks involved to be conserved (Fig. 2).

It is generally accepted now that fluctuations in pH around a value of about 9 are a major controlling factor of silica precipitation (Siever, 1962). When the pH exceeds 9, the solubility of silica increases dramatically; if the pH then falls to a lower value, it is precipitated. An inverse solubility relationship exists between calcite and silica at high pH (over 9), favouring calcite precipitation and the dissolution of silica (Fig. 3); the situation is, however, reversed at slightly lower pH.

Experimental studies on the replacement of carbonate minerals by silica are scarce. Lovering and Pattern (1962) reported that solutions supersaturated with respect to opal A undergo a fall in their pH from 6.8-7.1 to 5.7-6.2 when brought into contact with CO_2 at 101.325 Pa pressure and room temperature. These solutions are capable of not only dissolving calcite and dolomite, but also of precipitating silica. Other experimental reactions (Bisque, 1962) clearly show the influence of the clay minerals included in the carbonate, since silica is stabilized in a continuous three-dimensional polymer which includes the clay fraction of the rock.

Hesse (1989) and Maliva and Siever (1989) reported three mechanisms for the replacement of carbonates by silica: (1) the production of CO_2 by the decomposition of organic matter, or CO_2 introduced into the waters by biological activity, results in a local lowering of the pH, affecting calcite solubility and inducing silica precipitation (Siever, 1962;

Knoll, 1985 among others); (2) oxidation of hydrogen sulphide, reducing the pH at oxic/anoxic boundaries (Clayton, 1986); and (3) the dissolution of calcite and the precipitation of silica via the mixing of marine and continental waters (Knauth, 1979). Part of the groundwater in the mixing zone can be simultaneously supersaturated with respect to quartz and opal, and undersaturated with respect to calcite. In continental environments, the same mechanism can occur in areas where saline-lake waters mix with meteoric groundwater (Nickel, 1982).

Maliva and Siever (1989) indicated, however, that none of these mechanisms explains why the volumetric rate of silica precipitation is equal to the calcite dissolution rate. These authors propose " the force of crystallization" to be responsible, in which the non-hydrostatic stress resulting from quartz and opal CT growth largely accounts for carbonate dissolution in solution films at silica/carbonate contacts.

Other important factors to be considered in silicification are the porosity of the carbonate rock and groundwater flow. Thiry and Ribet (1999) proposed a mathematical model (reaction-transport) to characterize the physico-chemical conditions necessary for groundwater silicification in continental limestones. This model suggests that the kinetics of quartz precipitation limit silica replacement, whereas the diffusion of the dissolved species from the replacement front towards the voids seems to limit calcite dissolution. The model predicts that silica deposition and calcite replacement can be completed in about 10,000 to 100,000 years. McBride et al. (1999) established that the shape of the silica nodules seems to be controlled by the nature of the silica supply. Spherical bodies form when silica is supplied by diffusion, whereas elongated forms develop when it is supplied by advection, the concretions becoming elongated in the direction of fluid flow. Microscopic observation showed that the migration of silica occurs along the cracks and voids of the carbonate rock and in inter- and intracrystalline pores, the resulting quartz growing in an isolated manner (islands of advance: Fig. 4) within the host-rock.

3. Burial diagenesis

The specific conditions under which silicification may occur in carbonates during shallow burial early diagenesis may be quite different from those reigning during later burial

stages. The presence of organic matter and of changes in pH and salinity are crucial, but are mainly seen in early diagenesis and telogenesis.

3.1 Early diagenesis in lacustrine environments

The contemporaneous formation of inorganic chert/opal rocks and carbonates is unusual in lacustrine environments, and only occurs when they are very rich in silica. The silica precipitates with fluctuations in pH and temperature (Peterson and von der Borch, 1965; Wheer and Textoris, 1978; Wells, 1983; Mahran, 1999). The early silicification of carbonates is most probable. Early diagenesis is conventionally considered to start after the sediment is slightly buried and protected from direct interactions with the lacustrine water, although not so deeply as to experience noticeable pressure and temperature effects.

3.1.1 Silica source

Most early silicification that takes place can be explained by the redistribution of biogenic silica (opal A) accumulated with the carbonate sediments; this is possible due to the greater instabability of biogenic opal than other forms of silica. The biogenic remains found are usually those of diatoms, small sponges and phytoliths; sporadically, chrysophytes, testate amoebae and Heliozoa are found in small numbers (Denys et al., 1998). Thus, settings with exceptionally biogenic opal-rich accumulations are the most appropriate for early silicification, e.g., lakes (from dilute to hypersaline) and swamp basins. Lacustrine carbonate sediments in active volcanic settings usually include important quantities of diatomites. Once the silica microfossils are incorporated into the carbonate sediment, their diagenesis begins, and dissolution does not cease while pore waters are undersaturated with silica. When the pore fluid is enriched with silica as a consequence of the selective dissolution of the most easily dissolved biogenic silica components, dissolution halts. The dissolved silica in the pore fluids approaches saturation with respect to quartz, opal CT, and rarely opal A. Under such conditions, organisms may be preserved as ghosts in the chert/opal bodies (zone of silica accumulation), but not in the carbonate host-rock. In other cases, the conservation of the biogenic silica is due to other causes. Deocampo and Ashley (1999) described perennial

spring-fed wetlands in an arid basin in the caldera of a large trachytic volcano in northern Tanzania, where the biogenic amorphous silica (phytoliths, diatoms, etc.) is conserved in local environments of low-pH pore waters due to input of organic acids and CO_2 from decaying organic matter. In carbonates associated with volcanic basins, the alteration of volcanic ash/rocks is also an important source of silica for silicification.

Other less common sources of silica include the dissolution of detrital silicates (Peterson and Von der Borch, 1965), the release of silica by clay transformations (Mahran, 1999), and even silica introduced by springs and seeps (De Wet and Hubert, 1989; Smith and Mason, 1991). Springs and seeps are more common in continental rift basins and volcanic regions.

3.1.2 Timing

The time of silicification can be established relative to the carbonate cementation and diagenesis of the carbonate host-rocks (Hesse, 1989). Some studies on this topic have been performed on marine carbonates, but very few have been undertaken on continental carbonates. Extrapolating the data for the former and combining the results with the existing data for the latter shows that the following ten examples of early silicification are the most clear.

(1) The preservation of features typical of lacustrine or palustrine environments such as organic matter, rootlets, burrows, laminations, all types of desiccation cracks, peloids etc.; these are largely obliterated in the surrounding carbonate host rock (Bustillo et al., 2002).

(2) Silica nodules growing prior to mudcrack formation due to the desiccation of the lake (Wells, 1983).

(3) Pore-filling silica phases precipitated before or during the formation of early carbonate cements (Namy, 1974).

(4) Silicification before aragonite to calcite transformations (Jacka, 1974; Wright et al., 2003). Lakes are home to gastropods, ostracods and other organisms with calcite and/or aragonite shells. Aragonite can also form oolites or primary precipitates. When the original

microstructure of aragonite is pseudomorphed, early silicification is evident in the silicified limestone.

(5) Silicification predating early dolomitization. The replacement of limestones by chert prior to dolomitization is shown by the preservation in the chert of many primary features that have been deleted in the dolostone.

(6) Silicification associated with early dedolomitization as a result of the input of meteoric water into a lake (Arenas et al., 1999). In their study, the latter authors indicate that, after syngenetic dolomitization of laminated and stromatolitic lacustrine carbonates, dedolomitization occurred and the silica textures (lutecite) formed on the dolomites were corroded by dedolomite.

(7) Chert clasts incorporated into younger sediments (reworked cherts). Southgate et al. (1989) described poorly sorted chert intraclast conglomerates covering erosive surfaces.

(8) Interstratal dewatering of silica rocks during early diagenesis to produce cracks, convolutions (Fig. 5), pinchouts, folds, and mushroom like structures (Gimenez-Montsant et al., 1999). Intraformational breccias are common in early diagenetic silica bodies.

(9) Silicification prior to significant burial. The preservation of features corresponding to early mechanical compaction, such as a low packing density of silicified oolitic limestones, or the preservation of the incipient fracturing of oolites, ostracod carapaces and other alochems define an early silicification.

(10) In some cases, differential compaction of carbonates occurs around the chert (Banks, 1970); silica nodules can harden quickly due to rapid dewatering and can become more resistant to compaction than carbonates. In addition, the complete induration of chert nodules within unconsolidated carbonates can generate fragile bodies that crack and become displaced in unconsolidated carbonates (Carozzi and Gerber, 1978). On other occasions, minor compaction features can be observed in early chert, whereas compaction is intense in its non-silicified carbonate equivalents (Bustillo et al., 2002).

Much silicification of continental carbonates is associated with the last parts of the regressive sequences in which lakes evolve from shallow to palustrine settings, and in which water-level fluctuations cause emergence of the carbonate sediments (Mahran, 1999; Bustillo et al., 2002). Silicification processes in carbonates are associated with palustrine environments since they occur in zones where relatively high concentrations of organic matter

are present (Knoll, 1985), e.g., where rotting vegetation, logs and woody plants lower the pH, favouring silica precipitation.

Stromatolites, oncolites and other microbial carbonates may be selectively silicified in continental carbonate sections, and in some cases exhibit ghost minerals and/or structures of the former carbonates (Nickel, 1982; De Wet and Hubert, 1989; Bustillo et al., 2002) (Fig. 6). If these relics do not occur, it is difficult to distinguish between direct silica biomineralization of a micro-organism and silicification of the microbial carbonates. The main organisms involved in microbial carbonates are bacteria and cyanobacteria, as well as small algae and fungi that participate in the growth of microbial biofilms and mats (Riding, 2000). Silicification is also promoted because of the negatively charged OH^- and carboxyl groups on microbial surfaces, which allow binding with silicic acid (Renaut et al., 1998). In addition, the diatom communities established in many biofilms provide an additional local source of silica when dissolved (Winsborough, 2000). Although some authors question whether microbially mediated silica precipitation occurs, it is difficult to explain the selective silicification of microbial carbonates without it. Perhaps small changes in pH and CO_2 content, biologically induced by photosynthesizing algae in biofilms (Woodruff et al., 1997), help the dissolution of calcite and the precipitation of silica. The silicification process must be very early, because biofilms are degraded at shallow depths in the sediment column (even at 0.5 cm according to Westall and Rince, 1994).

In alkaline lake environments, cherts are associated with dolomites in saline mudflats, shallow lakes and ponds. This can be explained because alkaline environments provide suitable chemical conditions for the dissolution of silicate minerals (and consequently the formation of fluids very rich in silica) and are also suitable for the precipitation of magnesium carbonates (Peterson and Von der Borch, 1965). In many cases, these cherts do not replace carbonates because they are Magadi cherts (White and Youngs, 1980; Southgate et al., 1989).

3.2 Intermediate and deep burial diagenetic settings (mesogenesis)

Mesogenesis is dominated by burial effects in which pore-filling solutions are isolated from the overlying water masses under meteoric influence (Morrow and McIlreath, 1990). During mesogenesis, silicification is less common than in surface environments, and data for continental carbonates in this setting are practically non-existent. The main reasons for this

reduced frequency are: (1) intraformational biogenic silica does not exist since the opal of siliceous microorganisms is either dissolved or completely recrystallized to quartz; and (2) normally, changes in pH of the pore fluids are not as common as in early diagenesis; organic matter is also less common.

The silicification history of continental carbonates can be complex because early diagenetic silica may be remobilized and reprecipitated during mesogenesis.

Occasionally, the timing of burial diagenesis can be recognized via its evident features, as well as others described in the study of marine carbonates:

(1) cherts associated with late fracturing;
(2) chert micronodules occurring along stylolites;
(3) cherts post-dating mechanical and chemical compaction: Maliva (2001) described burial diagenetic cherts in marine carbonates after finding quartz crystals that cross-cut the concave-convex grain boundaries of oolites, and in facies of silicified stromatolites this author also reports stylolites showing altered subparallel lamination due to compaction-induced flow;

(4) silicification following burial dolomitization or dedolomitization.

Burial-diagenetic silica can be supplied by different sources. In silicification during the intermediate stages of burial diagenesis, the pressure solution of quartz and the transformation of smectite to illite have both been invoked as silica sources (Hesse, 1987). In general, silica-rich diagenetic fluids are a product of diagenetic reactions among silicate minerals, such as desorption and the decomplexing of silica bonds and/or clay-mineral alteration and recrystallization (Maliva, 2001). Clays and/or carbonates, in combination with an increasing burial temperature, act to keep the degree of silica saturation in the pore water low, providing conditions suited to slow quartz precipitation. An increase in pressure would also increase the solubility of the silica, but the degree of change would be small compared to that associated with temperature (Williams and Crerar, 1985). In some cases, the silica source is extraformational to the carbonates, sometimes associated with major hydrothermal and/or tectonic events, although this is more often seen in marine settings.

4. Meteoric diagenesis at or near the surface

4.1 Silcretes on lacustrine/palustrine carbonate deposits

Silcretes or siliceous duricrusts are defined by Summerfield (1983) as the indurated products of surficial and penesurficial silica accumulation. They are formed by cementation and/or low-temperature replacements of all types of rocks and sediments.

Pedogenic silcretes may form in a vadose environment by intermittent phases of leaching, infiltration and illuviation alternating with evaporation, whereas the formation of groundwater silcretes is related to silica transport driven by fluctuating water tables or lateral groundwater flows (Thiry and Milnes, 1991). In addition, silica deposition can occur at the interface of rising silica-rich groundwaters and less alkaline, percolating waters (Smale, 1973; Arakel et al., 1989). A recent review on silcretes (Nash and Ullyott, 2007) compiles many data on the different genetic and geomorphological types of silcrete. The pan/lacustrine geomorphological type, which often develops next to ephemeral lakes, pans or playas within endorreic basins, is frequently associated with shallow lacustrine and palustrine carbonates.

Pedogenic silcretes can occur where carbonate deposition is more or less regularly interrupted by episodes of non-deposition and subaerial exposure. Data for Late Quaternary shallow carbonates and silicification processes suggest that, in shallow environments, early-burial-diagenetic silica and pedogenic silica can appear together in a short time. Mees (2002) described such a case in pans of east-central Namibia with lacustrine carbonate deposits along their margins (micrites with ostracods, diatom and charophyte remains). In these carbonate deposits, early-diagenetic processes include the formation of amorphous silica nodules, in some cases, formed by the dissolution of diatoms and the reprecipitation of opal A. Late-diagenetic features produce various forms of secondary calcite and silica, some of them associated with bioturbation channels and planar voids or cracks.

Phytoliths are regarded as the major source of available silica in soils, although diatoms and even sponge spicules may be present (Clarke, 2003). When they dissolve, the silicic acid is precipitated primarily as opal A. Also, volcanic ash, which contains poorly ordered silicate glass, is susceptible to rapid dissolution.

Important silica precipitation may also take place when water evaporates from plants (Sommer et al., 2006) if the resulting Si concentration exceeds the solubility limit of the pore water. In this environment, microbial activity may mediate silica precipitation. While studying sedimentation and the formation of silcretes in the distal reaches of the Okavango Fan (Botswana), McCarthy and Ellery (1995) showed the accumulation of silica to be due to (1) phytoliths mixed with the substrate by illuviation and bioturbation, and (2) the

precipitation of fine-grained amorphous silica from the groundwater induced by the transpiration of rooted plants, plus increases in salinity. The accumulation of silica in the soil produces proto-silcretes.

Groundwater silcretes conserve the structure and texture of the carbonate host-rock. When the limestone is pure and without clayey layers, any silica present must arrive from other siliceous formations introduced by groundwater flow. Thiry and Ribet (1999) indicated that, due to the weak solubility of silica in surficial waters, a substantial groundwater flow is needed to supply the silica precipitated from solution, thus explaining the relationship between silicification and limestone porosity. The low silica concentration of the majority of groundwaters may explain why many groundwater silcretes are formed directly from quartz without an intermediate opaline phase. Banks (1970) proposed a model of the silicification of limestone in the water table as consequence of artesian upwelling and evaporative concentration. Other silica precipitation and carbonate dissolution sites include areas where different groundwaters mix with more saline fluids in playas.

4.2 Calcrete/dolocrete-silcrete associations

Calcrete/dolocrete-silcrete associations and silicified calcretes/dolocretes (Fig. 1C-D) occur in continental basins with arid or semi-arid climates (a.o., Watts, 1980; Summerfield, 1982; Meyer, 1987; Khalaf, 1988; Arakel et al., 1989; Armenteros et al., 1995; Nash and Shaw 1998); their formation is controlled by the pH, evaporation and salinity of the pore fluids.

The silicification of calcretes is widespread because the release of silica is an integral part of calcrete/dolocrete formation when it involves the replacement of silicates (Watts, 1980; Khalaf, 1988). This process is responsible for the enrichment of vadose or groundwater with silica, and can therefore provoke the development of silcrete. In addition to the silica obtained by the replacement of silicates, potential local silica sources include opal phytoliths and diatoms. Remote sources include silica-rich groundwaters (Summerfield, 1982).

The position of the silcrete in relation to calcrete/dolocrete can vary and is largely unpredictable (Summerfield, 1982). The silica volume accumulated is also variable. Watts (1980) reported that the silica derived from the calcitization of siliclastic components migrates downward to accumulate in lower calcrete horizons, but in areas where there is a lack of

drainage, calcrete may be intimately associated with silcrete (Smale, 1978). In some cases, the silica minerals only occur as void-filling cements in dolocretes or calcretes (Spötl and Wright, 1992; Nash and McLaren, 2003), but frequently silica void fillings occur alongside an appreciable replacement of carbonate minerals (Armenteros et al., 1995; Nash and Shaw, 1998). Lang et al. (1990) described a sequence of calcitization-palygorskitization-dolomitization-silicification that characterizes "sedimentation-calcretization cycles." These associations of processes are common in the closed continental Tertiary basins of Spain during arid to semi-arid timespans.

Arakel et al. (1989) described silcrete/calcrete cogenesis and the silicification of calcretes during the Quaternary in an arid zone of Australia. This author's descriptions and interpretations are interesting because the processes involved are relatively easily observed. The calcrete groundwater is slightly alkaline and oxidizing, and its temperature in the calcrete averages 25 ºC. Its silica concentration is in the range 25-100 mg/dm^3 over a range of salinity up to 100 g/dm^3. In the capillary fringe zone of the calcrete deposits, silica fills cavities, lines solution pipes, and cements irregular joint networks in brecciated calcrete. In the groundwater fluctuation zone, silica cements are also important but replacements of calcite by opal and quartz are more significant. In the vadose zone of the calcrete, salinity levels remain sufficiently high to promote the precipitation of silica from downward percolating pore solutions. In the groundwater level fluctuation zone, fluctuations in the pH due to freshening caused by meteoric water percolating through the soil capillary zone, plus surface evaporation, favour notable opal precipitation.

The study of the silicified calcretes of the Kalahari beds has provided important data since the processes involved are relatively recent (Plio-Pleistocene) (Summerfield, 1982). According to this author, the role of evaporation in silica precipitation is restricted to a zone close to the surface, whereas changes in pH dominate the control of calcrete replacement. The patchy silicification of calcretes is caused by either downward percolating waters or groundwater movements. Nash and Shaw (1998) described a chemically precipitated crust comprising a mixture of silica and $CaCO_3$ ("intergrade duricrust") and identify the major silica/carbonate relationships within intergrade duricrust types from the Kalahari of Botswana and Namibia. Three main intergrade types are identified on the basis of silica/carbonate associations: a calcrete containing secondary silica cement or silica replacing carbonates (sil-calcrete), a silcrete containing secondary calcite, and a duricrust in which silica and carbonate matrix cements appear to have precipitated contemporaneously in a close succession. The

silicification of calcretes is more extensive when replacement is related to groundwater fluctuations, or in upper sections where periodic flooding by ephemeral surface water occurs (Nash et al., 2004). In the Moshaweng Dry Valley, Botswana, Ringrose et al. (2002) described the formation of calcretes and sil-calcretes with the silicification of nodular calcretes during the mid- Pleistocene. After early calcrete formation on sands, the geochemistry of the hydraulic system changed and became increasingly saline, leading to silicification.

4.3 Early and late silcretes, and the time needed for silcrete formation

Early silcretes are formed rapidly after the sedimentation of carbonates or the formation of calcretes/dolocretes. Successive stages of silicification sometimes permit the penecontemporaneous reworking of earlier-formed silcrete and the incorporation of silcrete "intraclasts." Late silcretes form on carbonate rocks that undergo significant diagenetic changes by burial or when the ages of the carbonate host rock and silcrete are very different.

The formation of silcretes must be fairly rapid, since it is unlikely that the hydrological and chemical conditions necessary for their formation have prevailed for long periods in geological history. Arakel et al. (1989) described Late Quaternary calcretes and indicated their silicification to have occurred rapidly near the surface. However, numerical data are scarce. Meyer and Pena Dos Reis (1984) indicated that fossil silcretes need 100,000 years to form in semi-arid environments. Ringrose et al. (2002) described the silicification of nodular calcretes in the detrital Kalahari Group of the Moshaweng Dry Valley. Thermoluminescence data for sil-calcretes suggest that they are at most 275,000 years old, while the calcretes may be a little older.

One of the most recent and rapidly formed proto-silcrete formations is that described by Gutiérrezz-Castorena et al. (2006). Only 100 years were needed to form silica duripans at Lake Texcoco, near Mexico City. The sediments of this lake are very rich in silica (known as "jaboncillo"), but carbonates appear only in the calcitic-opaline ooliths associated with the lake's beaches. The lake was artificially drained in the 20th century. Following the emergence of the sediments about 100 years ago, a translocation of silica gave rise to the formation of different pedogenic types of opaline coatings and infilling, resulting in a local duripan.

4.4 Silicification of carbonate cave deposits

The silicification of carbonate speleothems occurs in typical carbonate karst caves, but also in volcanic tubes, sandstones and metamorphic caves. When siliceous solutions penetrate a karst along fractures or other voids, the silicification of carbonate cave deposits can occur. As well as extraformational silica, local sources may be available, such as diatoms forming part of carbonate speleothems (these generally grow close to the natural openings of caves).

Thin bands of calcite replaced by silica in the speleothems have been interpreted as evidence of pH fluctuations (Hill and Forti, 1997). However, other factors are also involved. The constant supply of water with silica and continuous evaporation can lead to silica supersaturation even with respect to opal. Woo et al. (2008) studied silicifications of "cave corals", defined as a variety of nodular, globular, botryoidal or coral-like speleothems, growing on the walls and floors of lava tubes on Jeju Island, Korea. When studying the silicification of those consisting of calcite and aragonite, these authors noted that the calcite layers were more susceptible to silicification. They suggested that impurities in the calcite layers (clays or organic matter) might facilitate this, and that the decay of the organic matter probably promotes local reductions in pH, leading to local silica saturation.

The Mescal Limestone of the Middle Proterozoic Apache Group in central Arizona, U.S.A., shows a palaeokarst which is one of the best preserved silicified karsts on Earth. It also hosts some of the best preserved Precambrian cave flowstones (Skotnicki and Knauth, 2007). The dissolution of the host carbonate allowed insoluble early-diagenetic cherts of the Mescal limestone to accumulate at their original stratigraphic level while the remaining carbonate underwent nearly complete replacement by secondary silica phases. These authors indicate that intense weathering of basalt lavas overlying the Mescal Limestone released abundant silica, leading to widespread silicification of the underlying palaeokarst. The geographic distribution of silicification was controlled by adjacent uplifting caused by movements along Precambrian monoclines.

4.5 Silicification of calcareous tufas and travertines

The diagenetic alteration of tufas and travertines consists primarily of the dissolution and precipitation of carbonates. The growing surfaces of calcareous tufa are dominated by diatoms, bacteria and cyanobacteria (Pedley, 2000) which may also mediate silica deposition. This scenario is similar to those described earlier involving stromatolites, oncolites and other microbial carbonates. Macrophyte stands (mosses, lichens, aquatic and marginal higher plants and trees) may comprise a significant part of the depositional framework (Pedley, 2000) and can be selectively silicified (Knoll, 1985).

In the calcareous deposits around hot springs, the circumstances are somewhat different because silica can be supplied by the thermal water, and the effect of temperature cannot be ignored. The silica supersaturation of the thermal fluid necessary for silica precipitation is achieved by its cooling when it reaches the surface. Calcite travertine coprecipitates with silica in some hot springs (Jones et al., 1996), but silicification does not always occur. Mixing and changes in the pH of the hydrothermal waters, evaporation and/or steam loss after discharge, could cause the silicification of continental carbonates formed in hot springs. Melezhik et al. (2004) described hot-water travertines with dolomite travertine crusts and mounds separated by internal dissolution surfaces, all veneered with 1-5 mm-thick crystalline silica sinters. The corrosive relationships between the dolomite travertines and the lower contact of the silica sinters, the desiccated and fragmented silica sinters, and the interlayered detrital sediments, suggest silicification occurred prior to burial.

5. Isotope data of cherts in continental carbonates

The oxygen- and, to a lesser extent, the hydrogen-isotope compositions of chert have been used to interpret environmental conditions; this is made possible due to the resistance of quartz to weathering and diagenesis. If cherts contain significant amounts of the mineral opal, the data obtained are unreliable since, during standard analysis, the water content of opal cannot be easily removed without exchanging water oxygen with the tetrahedrally-bound silicate oxygen (Knauth, 1992). According to the latter author, opal may not have regular enough Si-O bonding to yield systematic isotopic fractionation.

$\delta^{18}O$ analyses examine the structural oxygen present (Si-O-Si), whereas the results of δD analyses reflect the isotopic composition of the OH sites in microcrystalline cherts (Knauth and Epstein, 1976; Sharp et al., 2002). Knauth (1992) indicated that the OH sites

correspond to hydroxyl hydrogen and H_2O trapped as microfluid inclusions derived from dehydration reactions between adjacent hydroxyl groups. If the quartz of the chert is formed directly during the replacement of the carbonates, the conditions defined are those that existed during silicification, but if the quartz is formed by the ageing of previous opal, the information obtained only refers to the process of recrystallization from opal.

The $\delta^{18}O$ composition of the cherts included in continental carbonates can be very variable. Indeed, important isotopic variability may exist within a single chert nodule. Larger nodules can show a composite pattern with many crystallization zones in different stages that involved different types of water (McBride et al., 1999). In contrast, a Palaeogene carbonate unit of the Tajo Basin, Madrid Basin, is home to composite nodules (Fig. 7) that show two stages of silicification but which have similar isotope values (Bustillo et al., 2002). The variability can be due to the following two factors.

(1) Changes in temperature during chert growth. The exact temperature of quartz formation cannot be well known because of uncertainties in the quartz/water fractionation (Knauth and Epstein, 1976), but a temperature range associated with the isotopic variability can be established assuming that the isotope composition of the fluids remained constant (Fig. 8). In burial diagenesis, the isotopic composition of the cherts can record the thermal history of the carbonate host-rock.

(2) Variability of the isotope composition of surface waters. Most of the silicification of continental carbonates occurs in surface environments; the $\delta^{18}O$ and δD of the quartz therefore record surface-water compositions that are strongly influenced by evaporation (Abruzzese et al., 2005). In plots of $\delta^{18}O$ vs. δ D, meteoric waters worldwide show a line with a slope of ~ 8 (the Global Meteoric Water Line, or GMWL). If the correlation line for the $\delta^{18}O$ and δD values of the cherts has a less steep slope than that of the GMWL, this may mean that intense evaporation occurred (Abruzzese et al., 2005) (Fig. 9). The latter authors studied the oxygen- and hydrogen-isotope composition of Eocene and Miocene fresh-water cherts in the western United States and found $\delta^{18}O$ values from 11.2 $^{0}/_{00}$ to 31.2 $^{0}/_{00}$ in cherts formed by early silicification of lacustrine limestones. This wide scatter of $\delta^{18}O$ and δD values is attributed to the evaporation of surface water. Regional climatic and topographic variations in the Cenozoic can be deduced from these isotope data.

Bustillo et al. (2002) analysed chert included in lacustrine and palustrine limestones in a Palaeogene carbonate unit, and found the isotope values of the cherts in palustrine

limestones to be higher than in lacustrine limestones, probably indicating the presence of more evaporitic formation waters.

The correlation between chert $\delta^{18}O$ and the $\delta^{18}O$ of adjacent carbonate is very interesting. Abruzzese et al. (2005) measured the oxygen-isotope composition of calcite in close association with chert nodules and found a positive correlation. This correlation supports the notion that the chert is an early-diagenetic feature likely to record surface conditions.

Sharp et al. (2002), who studied the isotopes of cherts in Jurassic marine limestones, offer other interpretations that can be extrapolated to lacustrine environments. According to these authors, when the silicification of limestone is synsedimentary to very early diagenetic, the growth of chert nodules records the conditions of the sedimentary basin. These authors indicate that the antiphase hydrogen- and oxygen-isotope periodicity found in chert nodules record the thermal history of a high-permeability sedimentary basin with hotter waters upwelling in certain areas.

6. Concluding remarks

For many years, the cherts and opaline bodies in continental carbonates have received little attention since their thickness and frequency are small in relation to carbonate layers. However, if the silica bodies formed are diagenetic, i.e., if they have been formed by the replacement of the associated carbonate rock, their study is important since many of the sedimentological and diagenetic features erased from the carbonate rocks by dissolution or diagenetic change are preserved in the silica rocks. Pseudomorphic replacement reproduces the features of the carbonate host-rock at the moment of the silicification. The conservation of such features is much better if the silica phase forms quartz directly (chert). Chert, due to its resistance to alteration and isotopic change, can be an excellent tool for deducing the circumstances of continental carbonate deposits and their diagenesis.

When silicification is early diagenetic or telogenetic, the record of variation in the oxygen- and hydrogen-isotope composition of the quartz reflects that of the terrestrial surface environment. Changes in the relationship between $\delta^{18}O$ and δD in chert allow the degree of evaporation of the surface waters to be deduced, and this can be related to the climatic and topographic changes occurring during silicification. Isotopic comparison of the continental carbonate host-rocks and the cherts included in them provide clues regarding climate changes.

Cherts formed during burial diagenesis can be an important tool for studying some of the chemical and physical transformations experienced by carbonates, and the $\delta^{18}O$ status of quartz can mark the thermal history of the carbonate host-rock.

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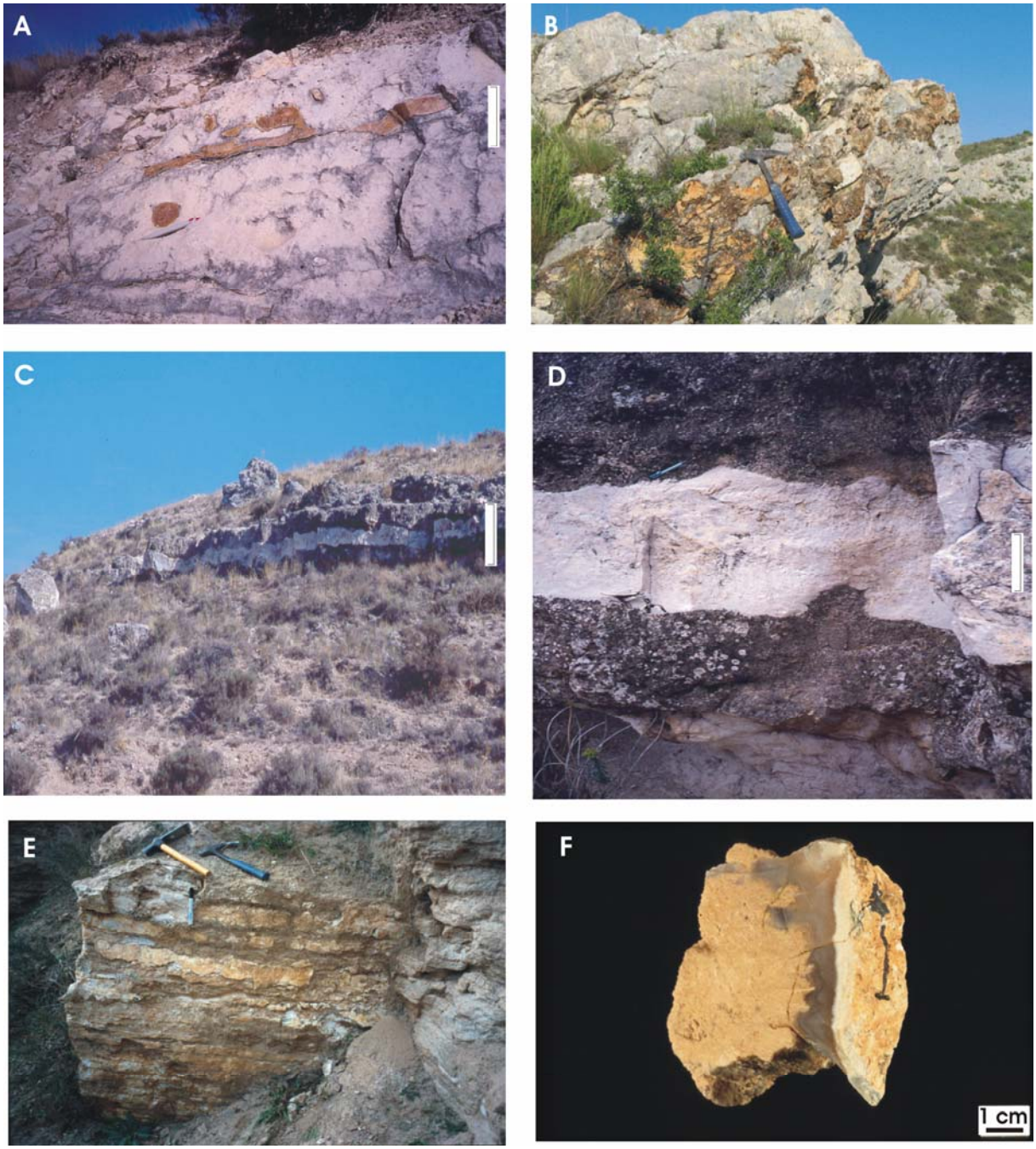

Fig. 1. Outcrops showing occurrences of silica rock formed by silicification of continental carbonates. **A**: Nodules and lenticular beds of chert in lacustrine/palustrine carbonates. Palaeogene. Torremocha de Jadraque, Tajo Basin, Spain. Scale bar 15 cm. **B**: Very irregular silicification of lacustrine limestone with gypsum. Palaeogene. Almazán Basin, Spain.C: Tabular opaline silcrete (white horizon) formed by silicification of a dolocrete (dark bed). Scale bar (on the duricrusts) 1.80 m. **D**: Close-up of both duricrusts with irregular contacts. The dolocrete is formed on an argillaceous bed (lower part of the picture). The maximum thickness of the silcrete in this picture (white horizon) is around 1 m. Scale bar 20 cm. Miocene. Maderuelo. Duero Basin, Spain. **E**: Silicification of successions formed of lacustrine limestones and gypsums. The face of the outcrop represents a fracture, and silicification has occurred along it. Silicification progressed from the fracture to the inside of

the host rock (see Fig. 1F). Miocene-Pliocene. Jumilla, Spain.**F**: Hand sample showing the progressive silicification mentioned in Figure 1E.

Fig. 2. Hand sample of a silicified palustrine limestone. In the silicified part (darker area), the bioturbation and brecciation of the palustrine host rock is clearly visible. Palaeogene. Torremocha de Jadraque, Tajo Basin, Spain. Scale bar 4 cm.

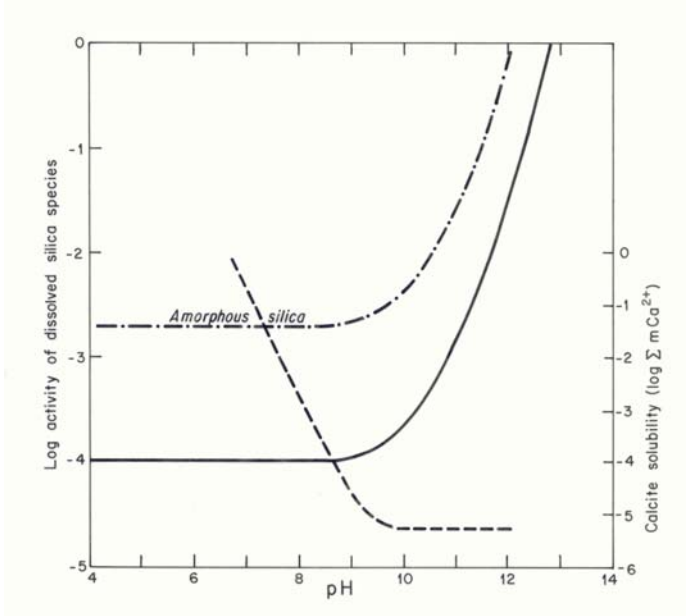

Fig. 3. Superposition of the solubility curves for the calcite and silica phases with respect to pH. The solubility curve for calcite at 25 ºC and atmospheric CO_2 pressure ($PCO_2 = 10^{1.5}$ Pas) (dashed line) is taken from Langmuir (1997). The solid line represents the total dissolved silica concentration in equilibrium with quartz. The remaining line is that for amorphous silica. The last two lines were obtained at 25 ºC (Drever, 1988).

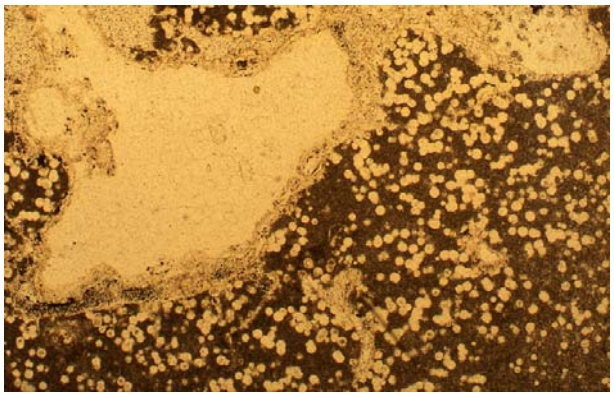

Fig. 4. Thin section showing centres of chalcedony (islands of advance) growing in an isolated fashion replacing a lacustrine micrite. The increase in the number of chalcedony centres forms a continuous mass of chert. Plane polarized light. Miocene. Madrid Basin. The width of the photomicrograph is 35 mm.

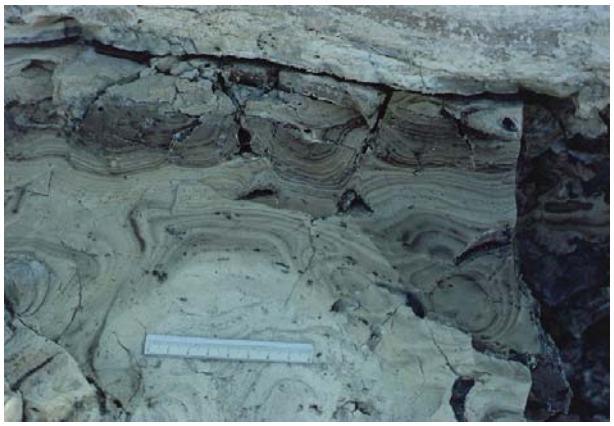

Fig. 5. Silicification at the top of a lacustrine limestone bed. Silicification formed opaline rock with a Liesegang structure. Dewatering of the opaline rock produced cracks and convolutions by which the original shape of the Liesegang structure was distorted. Villaluenga, Miocene, Madrid Basin.

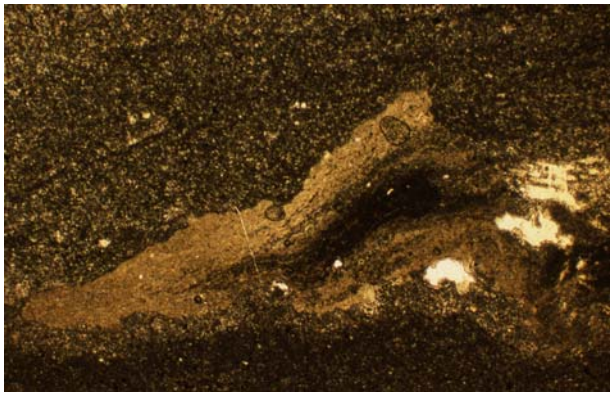

Fig. 6. Selective silicification of a small microbial bioconstruction in a lacustrine micrite. Relics of the carbonate lamina occur in the silicified (clear) part. Villaluenga. Miocene. Madrid Basin. The width of the photomicrograph is 35 mm.

Fig. 7. Composite nodule. The inner part is formed by microquartz and shows vertical millimetric bioturbation channels. The outer part is formed by megaquartz and encloses many relics of the carbonate host-rock. Double nodules reveal two stages of silicification that involved similar meteoric waters (Bustillo et al., 2002). Scale bar 3 cm.

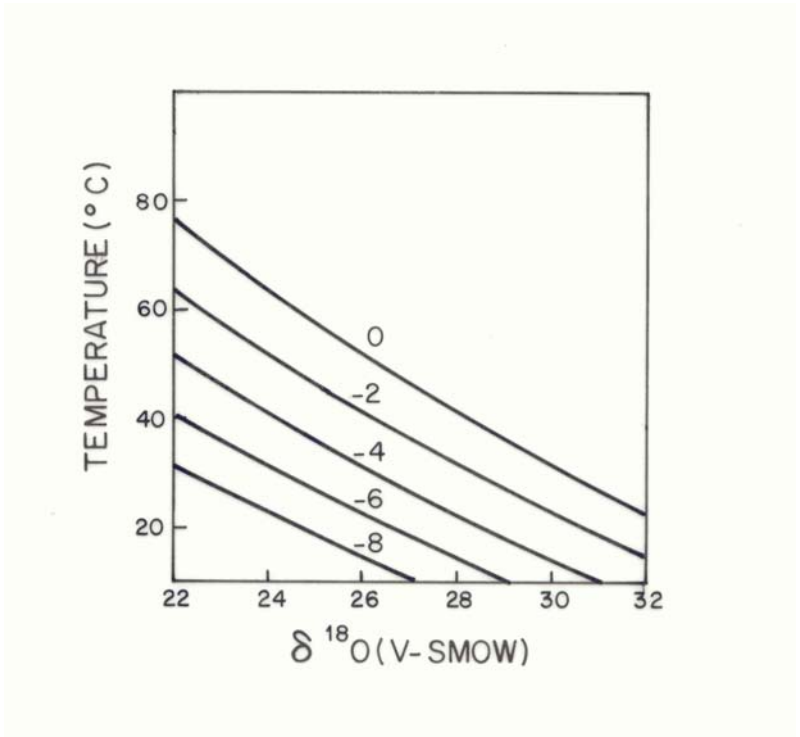

Fig. 8. Temperature against $\delta^{18}O$ values for cherts that formed in pore waters with $\delta^{18}O$ values of 0, -2, -4, -6 and -8 $^{0}/_{00}$ (reported relative to “Standard Mean Ocean Water" SMOW), according to the equation of Knauth and Epstein (1976).

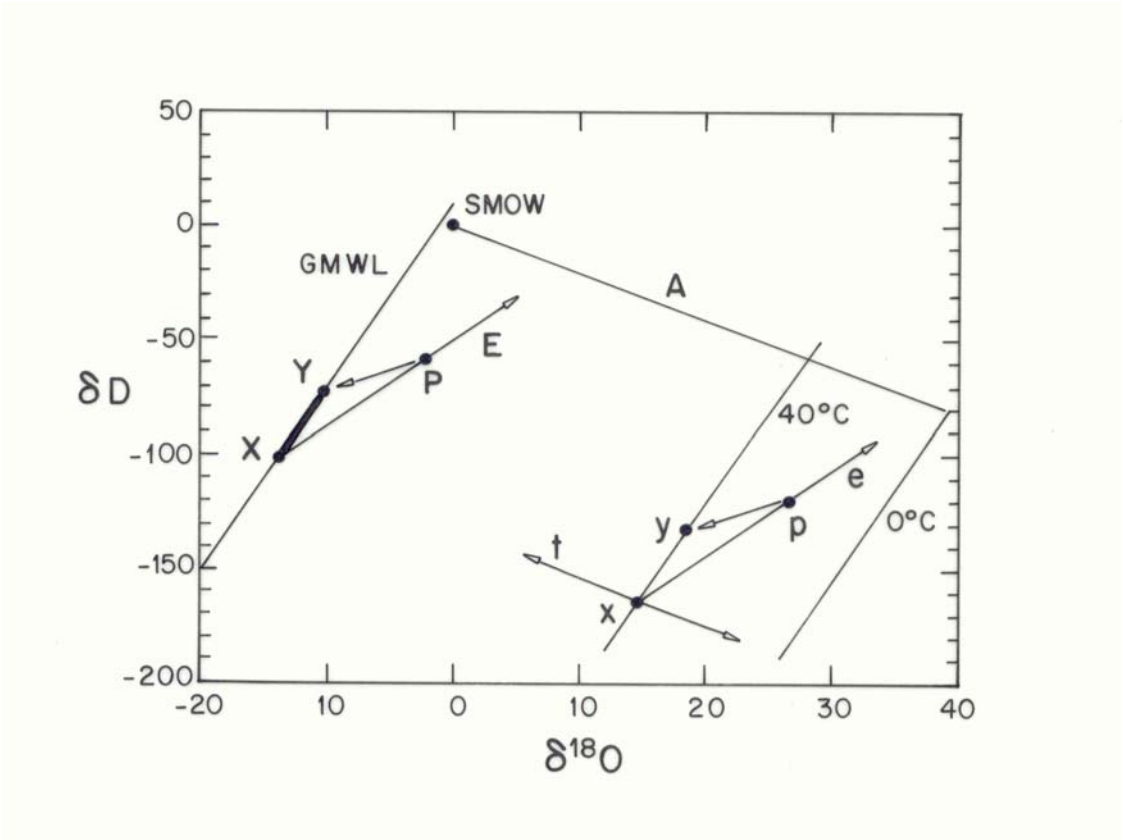

Fig. 9. Anticipated evolution of the isotope composition of water and chert in equilibrium. Cherts in equilibrium with meteoric water at different temperatures define domains parallel to the Global Meteoric Water Line (GMWL); the 0 °C and 40 °C lines are examples. Chert that forms in water with composition X at 40 °C has a composition x, connected by a chord with the slope of line A (Knauth and Epstein, 1976; Sharp et al., 2002). At different temperatures, the composition of chert would lie along line t. Evaporation of water X causes the remaining water to evolve along line E (and chert compositions along line e). If, at point P in this process, the water is then mixed with meteoric water of composition Y, the resulting isotope compositions will lie along line PY with a very low slope, and cherts forming in such waters would define line py. The thick line XY would represent the actual range of lake-water compositions from which the chert formed, even though the $\delta^{18}O$ alone of p, for example, would suggest isotopically heavier water. From Abruzzesse et al.'s (2005) figure 8.